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The Photochemistry of 3,3-Dialkoxy-1-phenylpropan-1-ones

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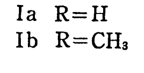
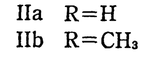
Synopsis. The irradiation of 3,3-dialkoxy-1-phenylpropan-1-ones (Ia-b) in a benzene solution afforded *β*-keto-esters (IIa-b), phenyl *β*-alkoxyvinyl ketones (IIIa-b), and tetrahydrofuranols (IVa-b).

The photoreaction of aliphatic ketones to give smaller ketones, olefins, and cyclobutanols has been widely studied.[1)] It is well established that the reaction proceeds *via* *γ*-hydrogen abstraction to give 1,4-diradicals which can either cleave to olefins, ring closure to cyclobutanols, or return to starting materials. Recently, the ultraviolet irradiation of *β*-alkoxy ketones has been reported to give the tetrahydrofuranols as the major product.[2–4)] They have been considered to arise *via* *δ*-hydrogen abstraction by excited carbonyl oxygen. We will report here on the photochemistry of 3,3-dialkoxy-1-phenylpropan-1-ones (Ia-b), which includes a new photooxidation (IIa-b) as well as photoelimination (IIIa-b) and *δ*-hydrogen abstraction (IVa-b).

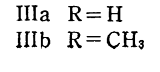
The irradiation of 3,3-dimethoxy-1-phenylpropan-1-one (Ia) in a benzene solution with a high-pressure mercury lamp through a Pyrex filter under nitrogen for 20 hr gave methyl benzoylacetate (IIa) (35%), phenyl *β*-methoxyvinyl ketone (IIIa) (6.5%), and 3-phenyl-3-hydroxy-5-methoxy-tetrahydrofuran (IVa) (5%). Compounds IIa and IIIa did not show any H-abstraction under further irradiation and were recovered almost quantitatively. The structures of IIa[5)] and IIIa[6)] were confirmed by a direct comparison with their authentic samples. The structure of IVa was elucidated using its physical data and by elemental analysis. The NMR spectrum showed two doublets of a doublet at δ 2.23 (J=13.5, J=1.8 Hz, 1H at C-4) and δ 2.49 (J=13.5, J=3.5 Hz, 1H at C-4), two doublets at δ 4.06 and 4.26 (J=10 Hz, 2H at C-2), a doublet of a doublet at δ 5.19 (J=1.8, J=3.5 Hz, 1H at C-5), a singlet at δ 3.40 (3H, $-OCH_3$), a broad singlet at δ 3.90 (1H, –OH, exchangable with D_2O), and the multiplet at δ 7.15—7.65 (5H) due to the aromatic protons. The IR spectrum exhibited bands at 3500 cm^{-1} due to the hydroxy group and at 1100 cm^{-1} attributable to the ether group. The mass spectrum displayed prominent peaks at *m/e* 176 (M^+-H_2O), 164 ($M^+-CH_2{=}O$), 144 ($M^+-(H_2O+MeOH)$), and 115 ($M^+-(H_2O+MeOH+CHO)$).



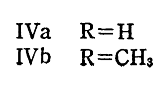
Ia R=H
Ib R=CH_3



IIa R=H
IIb R=CH_3



IIIa R=H
IIIb R=CH_3



IVa R=H
IVb R=CH_3

Similarly, ethyl benzoyl acetate (IIb), phenyl *β*-ethoxyvinyl ketone (IIIb), and 2-methyl-3-phenyl-3-hydroxy-5-ethoxy-tetrahydrofuran (IVb) were obtained in 15, 15, and 6% yield respectively by the irradiation of 3,3-diethoxy-1-phenylpropan-1-one (Ib). The structures of IIb[5)] and IIIb[7)] were confirmed by a direct comparison with their authentic samples, while that of IVb was elucidated by means of its spectral data and by elemental analysis.

The formation of IIa-b is presumed to proceed through the oxidation of Ia-b by light. The formation of IIIa-b can be explained by the elimination of the alcohol.[8)] On the other hand, the formation of IVa-b is considered to arise *via* *δ*-hydrogen abstraction by an excited carbonyl through a seven-membered ring transition state.

Experimental

All the boiling points are uncorrected.

The 3,3-dimethoxy-1-phenylpropan-1-one (Ia, bp 175—178 °C/20 mmHg (lit,[9)] 111—111.5 °C/2 mmHg)) and 3,3-diethoxy-1-phenylpropan-1-one (Ib, bp 165—170 °C/20 mmHg (lit,[10)] 111—112 °C/1 mmHg)) were prepared according to the methods of previous reports.

Irradiation of Ia. A solution of 1g of Ia in 150 ml of benzene was irradiated with a high-pressure merucry lamp through a Pyrex filter under nitrogen for 20 hr at room temperature. After irradiation, the benzene was evaporated *in vacuo*, and the residue was chromatographed on a silica gel column with benzene–ethyl acetate(50 : 1) to give 350 mg of methyl benzoyl acetate (IIa; bp 155—158 °C/20 mmHg (lit,[5)] 152 °C/15 mmHg)), 65 mg of phenyl *β*-methoxyvinyl ketone (IIIa; bp 114—117 °C/2 mmHg (lit.[6)] 135 °C/5—6 mmHg)), 50 mg of 3-phenyl-3-hydroxy-5-methoxy-tetrahydrofuran (IVa), and 50 mg of the recovered ketone.

3-Phenyl-3-hydroxy-5-methoxy-tetrahygrofuran (IVa): Bp 80 °C/2 mmHg. IR: ν_{max}^{film} cm^{-1}, 3500, 3050, 2830, 1600, 1492, 1100, 750, 690. Found: C, 67.77; H, 7.18%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%.

Irradiation of Ib. A solution of 1 g of Ib in 150 ml of benzene was irradiated under the same conditions as have been described above for 20 hr. After the removal of the solvent, the residue was chromatographed on a silica gel column with benzene–ethyl acetate (30 : 1) to give 150 mg of ethyl benzoylacetate (IIb; bp 152—158 °C/18 mmHg (lit.[5)] 147 °C/11 mmHg)), 150 mg of phenyl *β*-ethoxyvinyl ketone (IIIb; bp 150—152 °C/20 mmHg (lit.[7)] 156—158 °C/28 mmHg)), 60 mg of 2-methyl-3-phenyl-3-hydroxy-5-ethoxy-tetrahydrofuran (IVb), and 100 mg of the recovered ketone.

2-Methyl-3-phenyl-3-hydroxy-5-ethoxy-tetrahydrofuran (IVb): bp 93 °C/2 mmHg. IR: ν_{max}^{film} cm^{-1}, 3500, 3050, 1603, 1492, 1100, 750, 690. NMR: (δ in $CDCl_3$) 1.25 (t, 3H, J=9 Hz, methyl), 1.20 (d, 3H, J=6.5 Hz, methyl), 2.25 (d, 1H, J=13.5 Hz, methylene at C-4) and 2.63 (dd, 1H, J=13.5, J=5 Hz, methylene at C-4), 3.2—4.1 (m, 2H, methylene), 4.23 (q, 1H, J=6.5 Hz, methine at C-2), 5.23 (d, 1H, J= 5 Hz, methine at C-5), 7.2—7.65 (m, 5H, aromatic protons). When the signal of the methyl protons at δ 1.25 was irradiated, the signal of the methylene protons of the ethoxy group appeared as two doublets at δ 3.49 and 3.91 with the same coupling constant of 9 Hz. This phenomenon is considered to arise from the restriction of free rotation by the weak interaction of hydroxy and ethoxy groups. Mass spectrum: *m/e* 204 (M^+-H_2O), 178 ($M^+-CH_3CH{=}O$), 158 ($M^+-H_2O+EtOH$)), 115 ($M^+-(H_2O+EtOH+CH_3C{=}O)$). Found: C, 70.16; H, 8.09%. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%.

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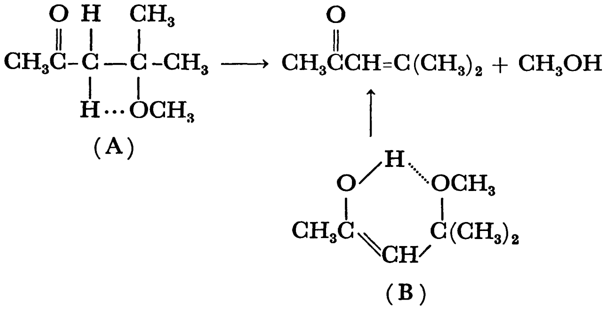

$$CH_3COCH=C(CH_3)_2 + CH_3OH$$

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